FT-ICR Ion Chemistry Lab Classes:

How to calculate reaction efficiencies and thermodynamic values from gas-phase kinetics

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«La sapienza»

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Outline

1. Calibration of pressure measurement
2. Collisional rate constant and reaction efficiency

3a. The thermokinetic method: gas-phase basicity

3b. The thermokinetic method: cation basicity

The pressure issue

$$k_{exp} = \frac{k_{obs}\,(s^{-1})}{[N]} = \frac{k_{obs}}{P(mbar)\ 2.4\ 10^{16}}$$

Unit conversion factor for T = 298 K

$[N]$ = concentration of neutral molecule in particle cm^{-3}

Correction factor from reference methane reaction

$$P(mbar) = \frac{P_{obs}(mbar)\ 1.62f}{R_x}$$

Relative responsiveness of the ion gauge to the volatile neutral

Choosing R_x

Vacuum/volume 33/number 3/pages 149 to 153/1983
Printed in Great Britain

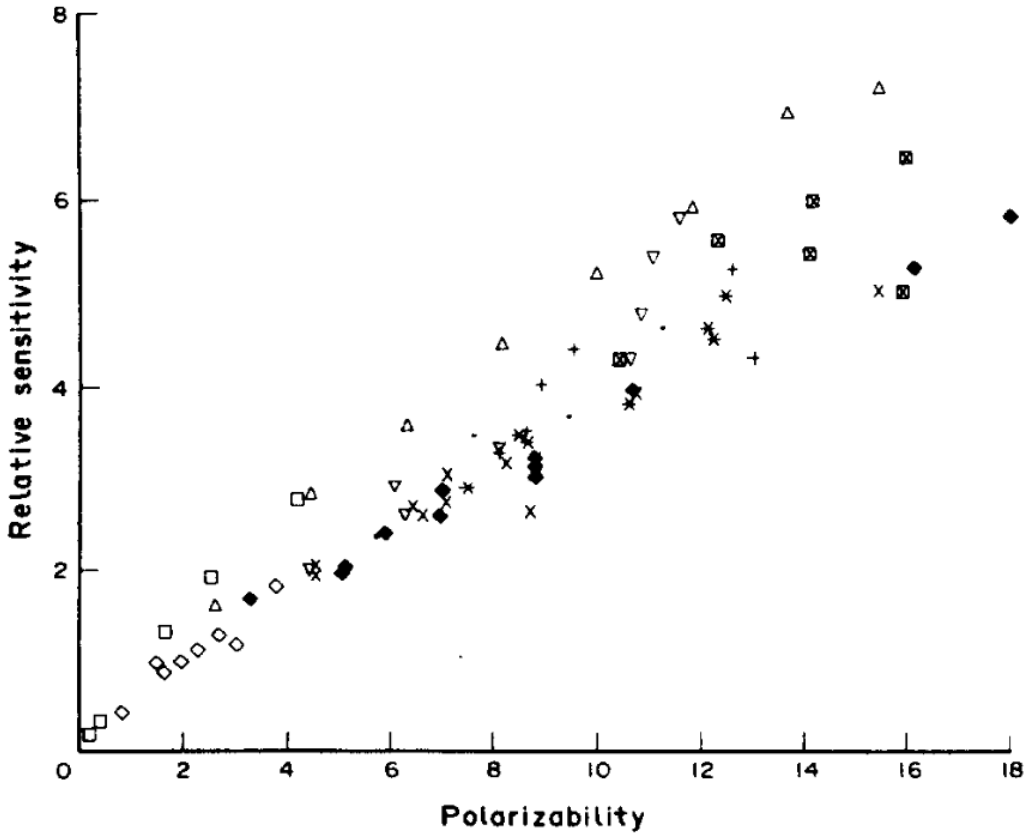
0042–207X/83/030149–05$03.00/0

Empirical methods for determination of ionization gauge relative sensitivities for different gases

John E Bartmess and Rosina M Georgiadis, *Department of Chemistry, Indiana University, Bloomington, IN 47405, USA*

received 4 February 1982

The relative sensitivities of a Bayard–Alpert ionization gauge for various organic molecules have been measured. There is a good correlation with total ionization cross section at 75 eV. For monofunctional compounds a correlation with number of electrons is seen with different functional groups on different lines. The best general correlation is with the polarizability, α, with $R_x = 0.36\alpha + 0.30$, where R_x is the chemical sensitivity relative to $N_2 = 1.00$. Alkanes and the noble gases have slightly larger R_x values than predicted by this equation.



Relative ion gauge sensitivities vs polarizability.

$$R_x = 0.36\alpha + 0.30$$

Values relative to $N_2 = 1.00$

Compound	R_x
H_2	0.44
He	0.33
Ar	1.32
H_2O	0.97
NH_3	1.12
O_2	0.87
N_2	(1.00)
CO_2	1.30
$(CH_3)_2CO$	2.50
CH_3CN	1.99
Pyridine	3.80
Me_2S	3.47
NO_2	1.30
$P(OMe_3)$	3.70
Chloroform	3.34
CH_4	1.62
Acetic acid	1.54
Benzene	4.29

The methane reaction

$$CH_4^{+\bullet} + CH_4 \xrightarrow{k_{ref}} CH_3^{\bullet} + CH_5^{+}$$

Known rate constant* = k_{ref} = 1.1 10^{-9} cm^3 s^{-1} $particle^{-1}$

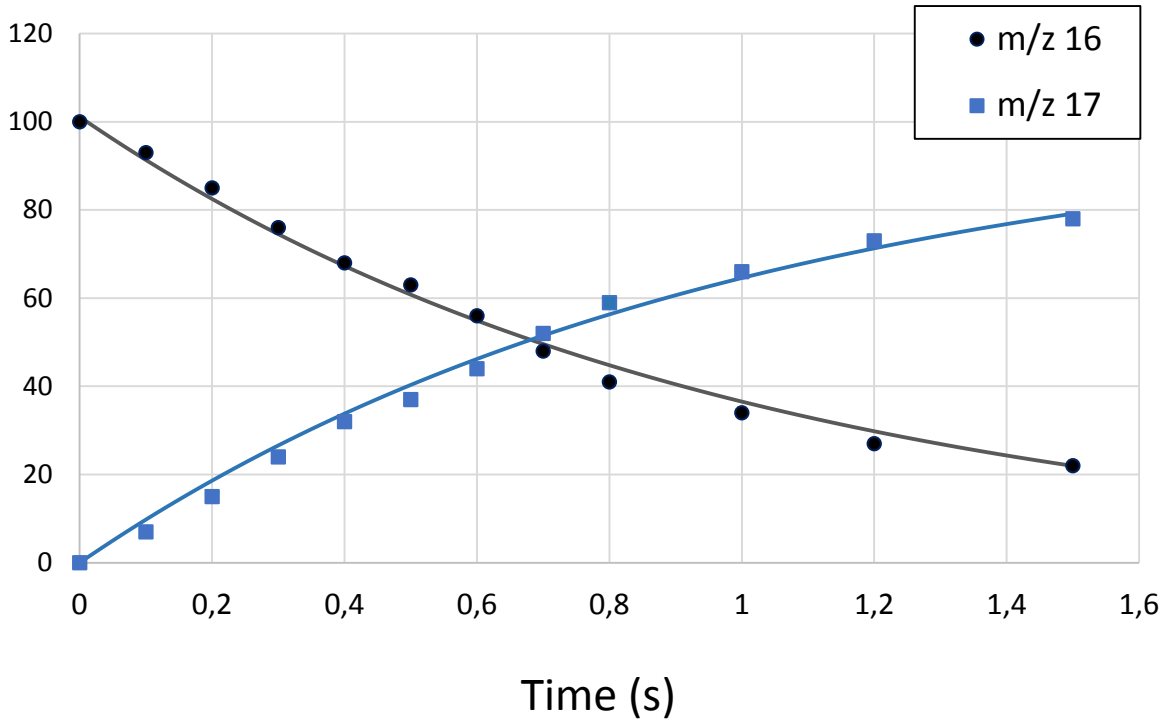
$$k_{ref} = \frac{k_{obs}}{[N]} = \frac{k_{obs} R_x}{P_{obs} 2.4\ 10^{16}\ 1.62 f} \longrightarrow f = \frac{k_{obs} R_x}{P_{obs} 2.4\ 10^{16}\ 1.62} \frac{1}{k_{ref}}$$

*Meot-Ner, M. In Gas Phase Ion Chemistry; Bowers, M. T. Ed.; Academic Press: New York, 1979; Vol. I, Chap. VI, pp 197–271

Time (s)	*m/z* 16	*m/z* 17
0	100	0
0.1	93	7
0.2	85	15
0.3	76	24
0.4	68	32
0.5	63	37
0.6	56	44
0.7	48	52
0.8	43	57
1	36	64
1.2	28	72
1.5	23	77

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_3^{\bullet} + CH_5^{+}$$

$P_{obs}\ (CH_4) = 1.8\ 10^{-8}$ mbar



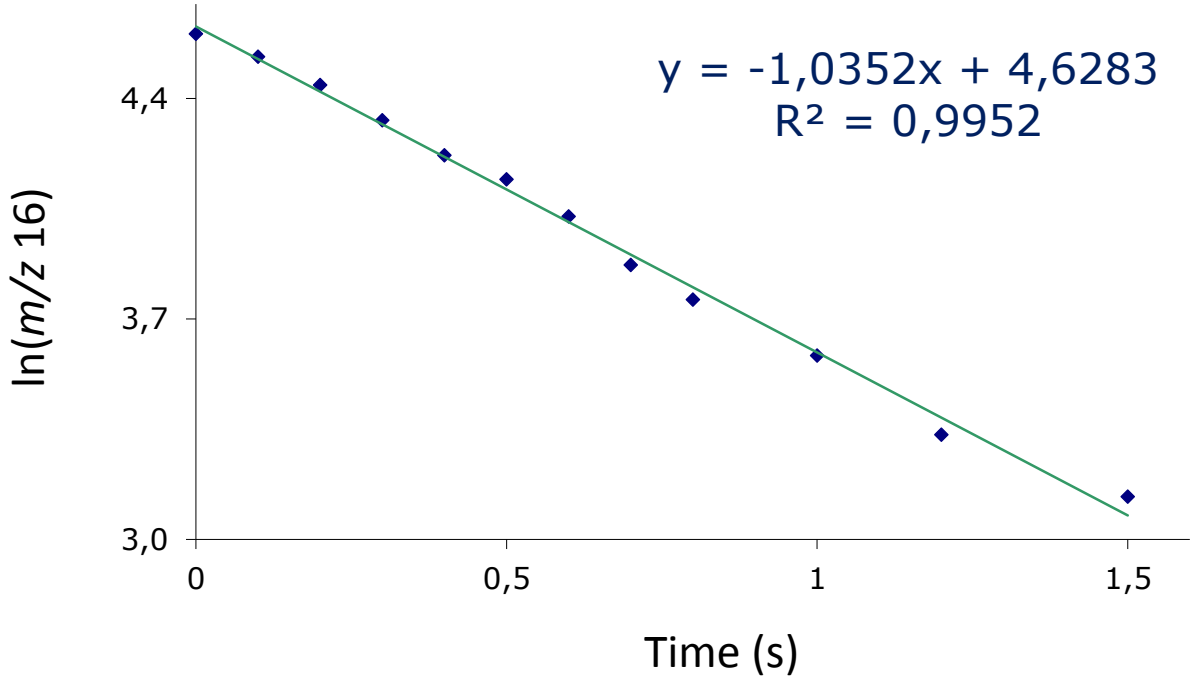
$k_{obs} = 1.0\ s^{-1}$

$$f = \frac{k_{obs}}{P_{obs} 2.4\ 10^{16}} \frac{1}{k_{ref}} = 2.2$$

Time (s)	*m/z* 16	*m/z* 17	ln(*m/z*16)
0	100	0	4.6
0.1	93	7	4.5
0.2	85	15	4.4
0.3	76	24	4.3
0.4	68	32	4.2
0.5	63	37	4.1
0.6	56	44	4.0
0.7	48	52	3.9
0.8	43	57	3.8
1	36	64	3.6
1.2	28	72	3.3
1.5	23	77	3.1

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_3^{\bullet} + CH_5^{+}$$

$P_{obs}\ (CH_4) = 1.8\ 10^{-8}$ mbar



$k_{obs} = 1.0\ s^{-1}$

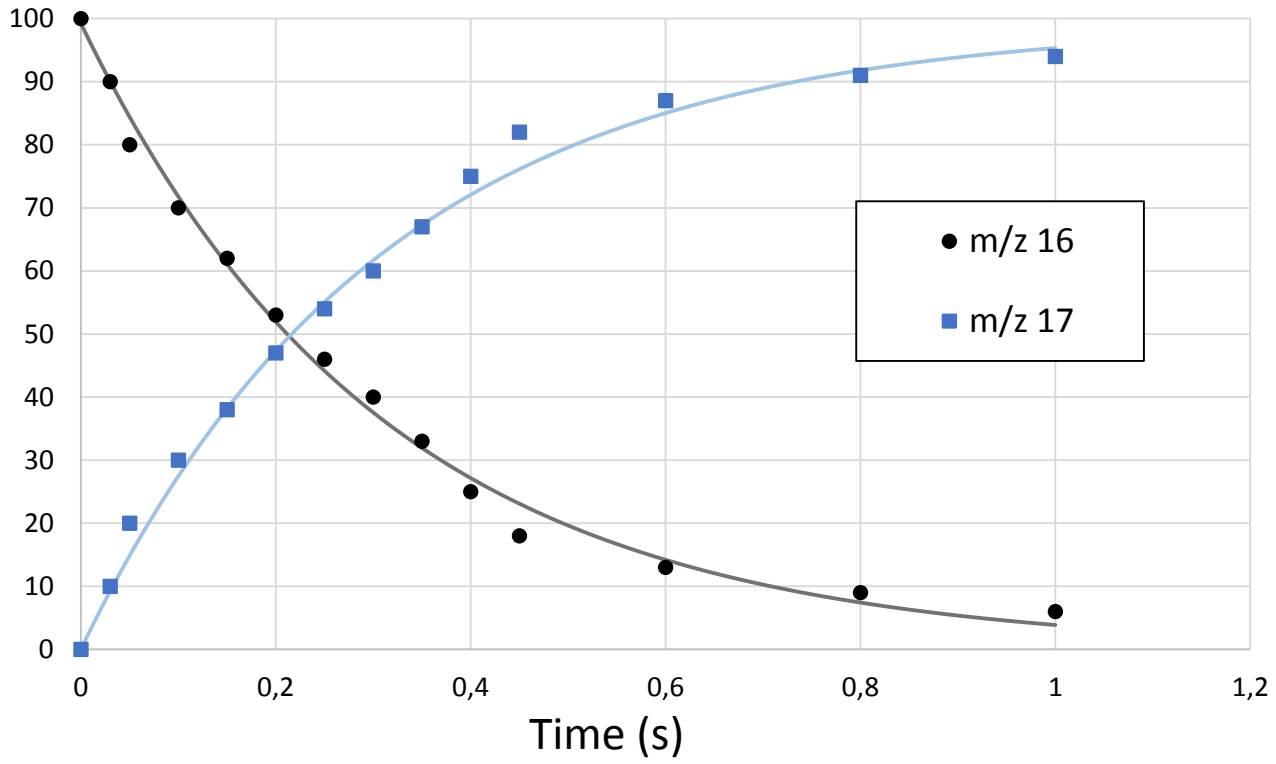
$$f = \frac{k_{obs}}{P_{obs} 2.4\ 10^{16}} \frac{1}{k_{ref}} = 2.2$$

Time (s)	m/z 16	m/z 17
0	95	5
0.02	88	12
0.04	79	21
0.06	71	29
0.08	65	35
0.1	59	41
0.12	52	48
0.14	47	53
0.16	44	56
0.18	39	61
0.2	34	66
0.3	24	76

$k_{obs} = 3.2\ s^{-1}$

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_3^{\bullet} + CH_5^{+}$$

$P_{obs}\ (CH_4) = 5.8\ 10^{-8}$ mbar

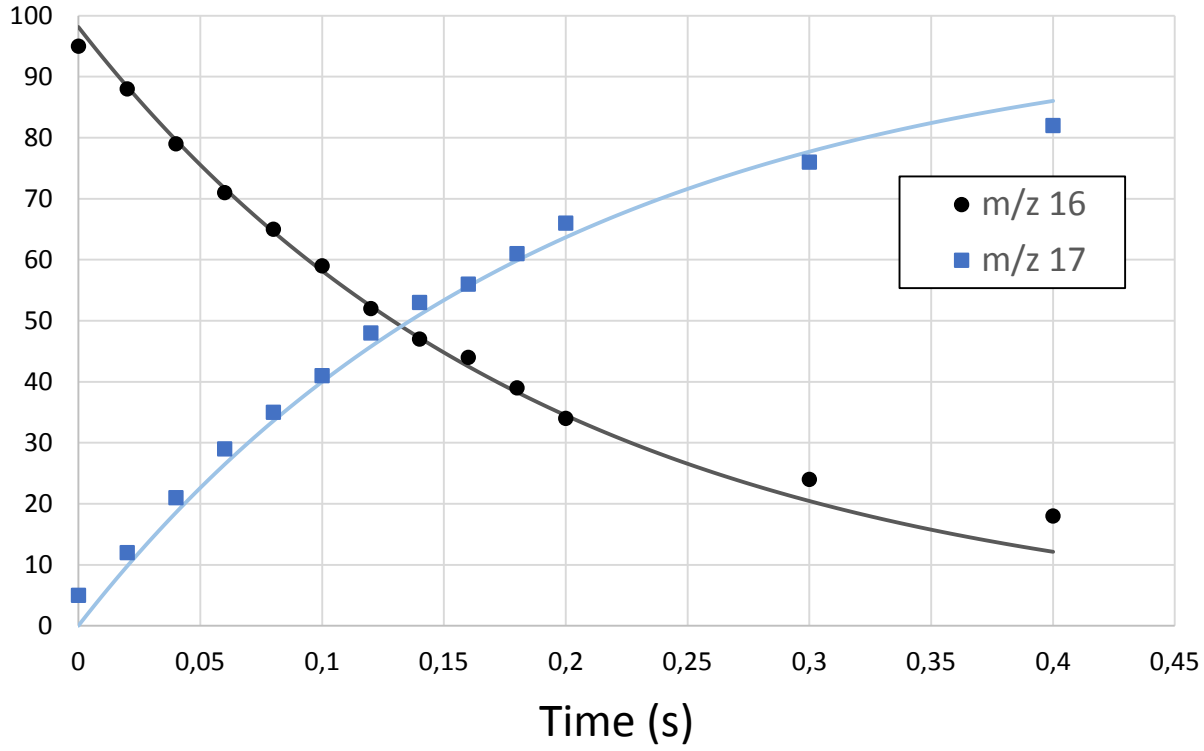


$$f = \frac{k_{obs}}{P_{obs} 2.4\ 10^{16}} \frac{1}{k_{ref}} = 2.1$$

Time (s)	m/z 16	m/z 17
0	95	5
0.02	88	12
0.04	79	21
0.06	71	29
0.08	65	35
0.1	59	41
0.12	52	48
0.14	47	53
0.16	44	56
0.18	39	61
0.2	34	66
0.3	24	76

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_3^{\bullet} + CH_5^{+}$$

$P_{obs}\ (CH_4) = 8.9\ 10^{-8}$ mbar



$k_{obs} = 5.2\ s^{-1}$

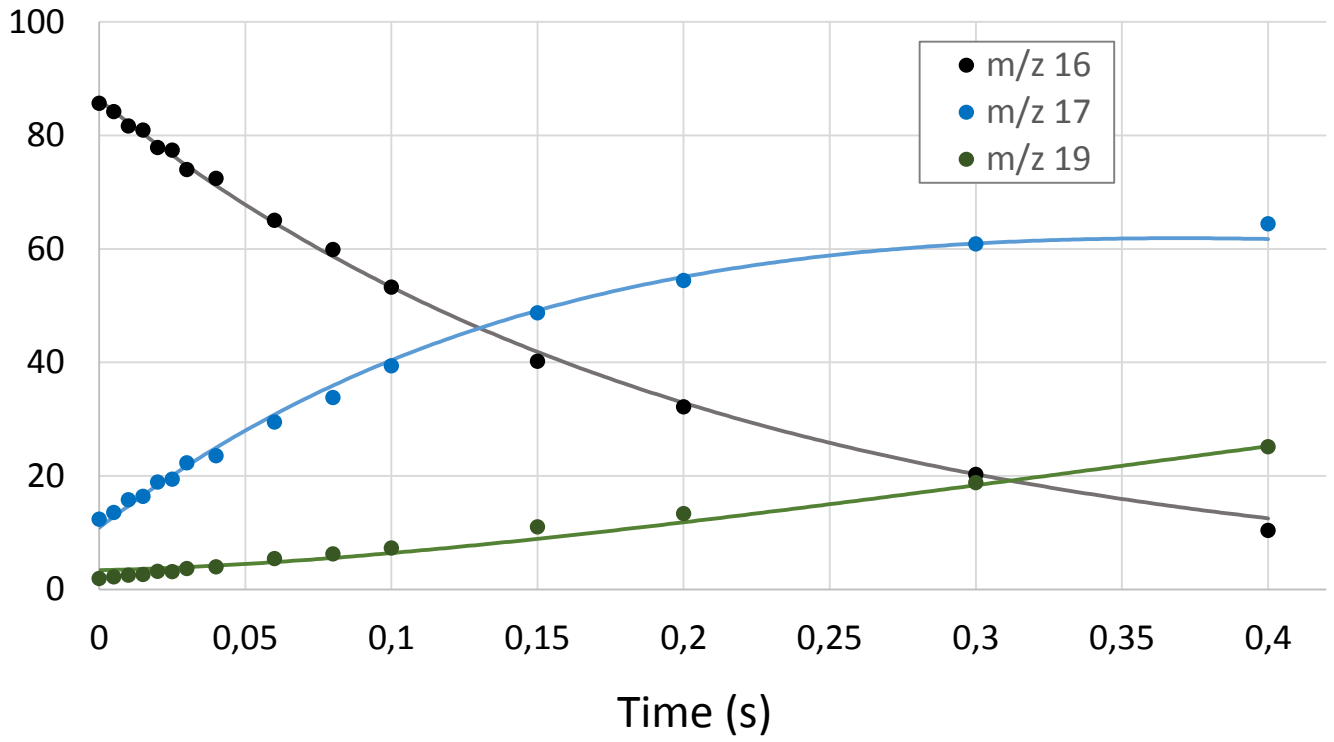
$$f = \frac{k_{obs}}{P_{obs} 2.4\ 10^{16}} \frac{1}{k_{ref}} = 2.2$$

Time (s)	m/z 16	m/z 17	m/z 19
0	85.67	12.39	1.94
0.005	84.21	13.57	2.22
0.01	81.67	15.81	2.52
0.015	80.95	16.41	2.64
0.02	77.88	18.93	3.20
0.025	77.42	19.44	3.15
0.03	73.99	22.32	3.69
0.04	72.45	23.57	3.99
0.06	65.05	29.51	5.44
0.08	59.91	33.82	6.27
0.1	53.28	39.41	7.31
0.15	40.22	48.75	11.03

$$CH_4^{+\bullet} + CH_4 \rightarrow CH_3^{\bullet} + CH_5^+$$

$$CH_5^+ + H_2O \rightarrow CH_4 + H_3O^+$$

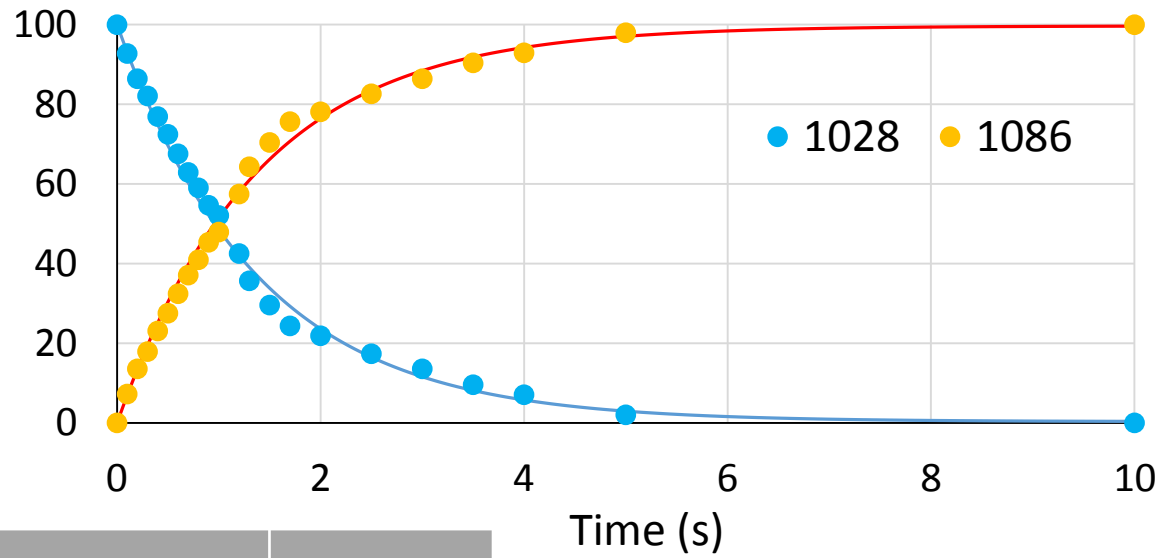
$P_{obs}\ (CH_4) = 1.2\ 10^{-7}$ mbar



$k_{obs} = 4.8\ s^{-1}$

$$f = \frac{k_{obs}}{P_{obs} 2.4\ 10^{16}} \frac{1}{k_{ref}} = 1.5$$

Calculation of bimolecular rate constant



Compound	R_x
NH_3	1.12
O_2	0.87
N_2	(1.00)
CO_2	1.30
$(CH_3)_2CO$	2.50
CH_3CN	1.99

$$[1028]^+ + [58] \xrightarrow{k_{obs}} [1086]^+$$

$[(TPFPP)Fe^{III}]^+$ Acetone

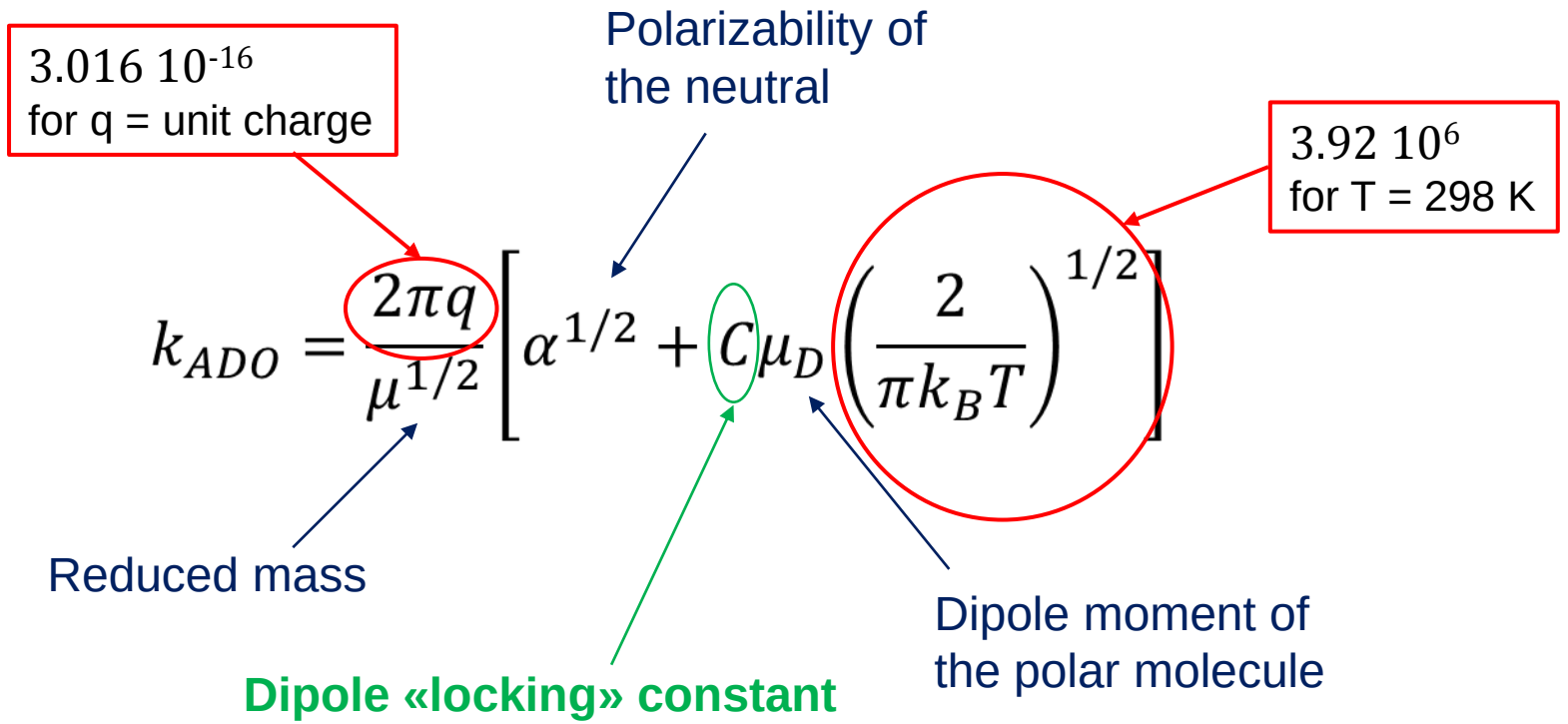
$$k_{obs} = 1.7\ s^{-1}$$

$P_{obs} = 4.3\ 10^{-8}$mbar ⟶ f = 2.11

$$k_{exp} = \frac{k_{obs}}{P} = \frac{k_{obs} R_x}{P_{obs}\ 2.4\ 10^{16}\ 1.62 f}$$

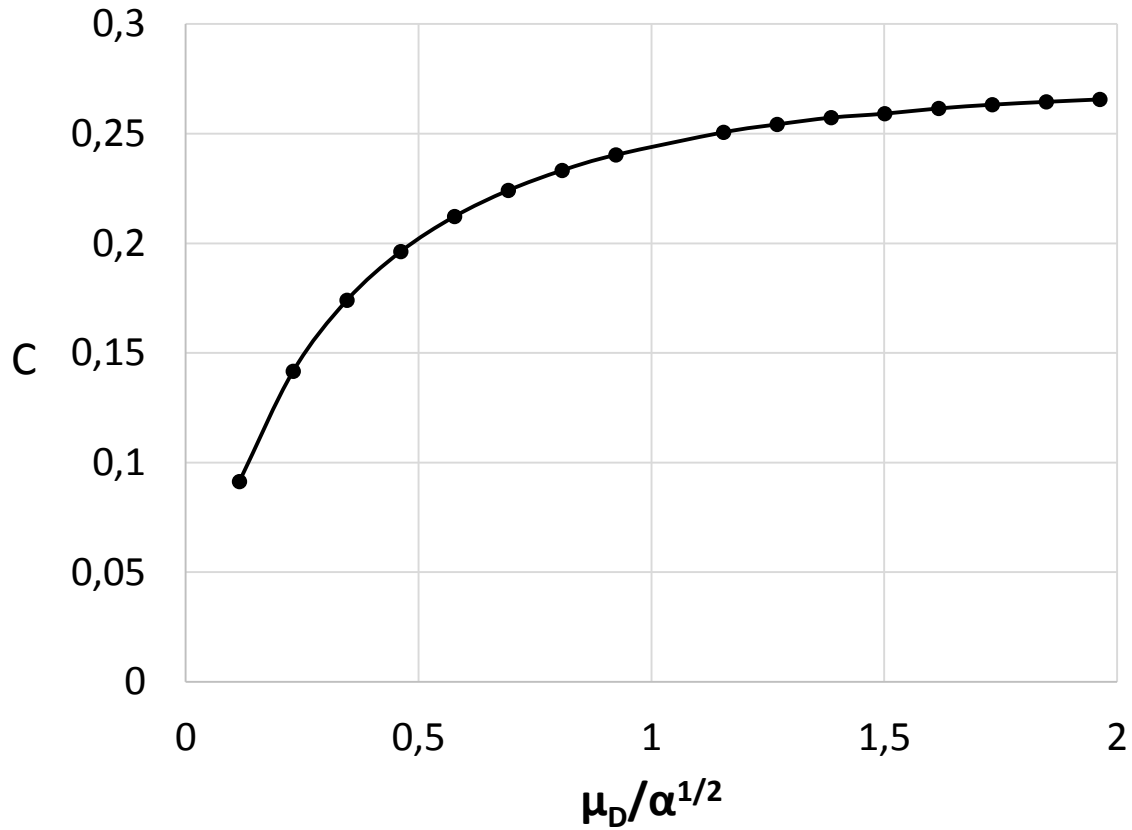
$$k_{exp} = 1.2\ 10^{-9}\ cm^3\ s^{-1}\ particle^{-1}$$

Calculation of k_{ADO}



Dipole «locking» constant

$\mu_D/\alpha^{1/2}$	C	$\mu_D/\alpha^{1/2}$	C
0.1155	0.0913	1.155	0.2506
0.2309	0.1416	1.270	0.2542
0.3464	0.1740	1.386	0.2573
0.4619	0.1962	1.501	0.2591
0.5774	0.2122	1.617	0.2615
0.6928	0.2241	1.732	0.2632
0.8083	0.2332	1.848	0.2645
0.9238	0.2403	1.963	0.2656



T. Su, E.C.F. Su, M.T. Bowers, J. Chem. Phys. 69 (1978) 2243–2250. doi:10.1063/1.436783.

Let's calculate the k_{ADO} of

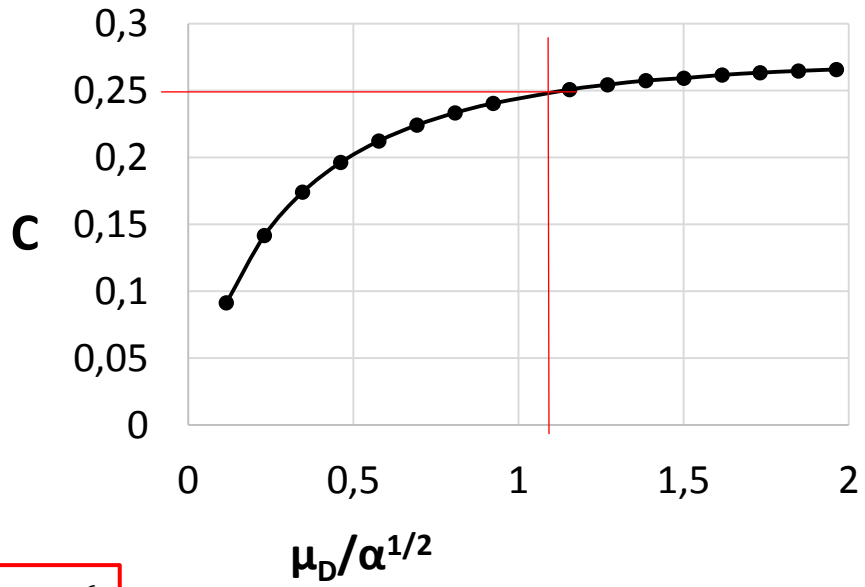
$$[(TPFPP)Fe^{III}]^{+} + [Acetone] \xrightarrow{k_{obs}} [(TPFPP)Fe^{III}(acetone$$

Care about units of measurement!!
k_{ADO}($cm^3\ s^{-1}$ $particle^{-1}$)

$\alpha = 6.41\ 10^{-24}\ cm^3$

$\mu = 9.17\ 10^{-23}\ g\ particle^{-1}$

$\mu_D = 2.85\ 10^{-18}\ C\ cm^{-1}$



$3.016\ 10^{-16}$

$3.92\ 10^{6}$

$$k_{ADO} = \frac{2\pi q}{\mu^{1/2}}\left[\alpha^{1/2} + C\mu_D\left(\frac{2}{\pi k_B T}\right)^{1/2}\right] = 1.7\ 10^{-9}\ cm^3\ s^{-1}\ particle^{-1}$$

What about the efficiency of the reaction?

$$\frac{k_{exp}}{k_{ADO}} = \Phi \longrightarrow \Phi = \frac{1.2\ 10^{-9}}{1.7\ 10^{-9}} = 0.71$$

Φ represents the fraction of collision events leading to products

The thermokinetic method

$A + H^+ \longrightarrow AH^+$

$-\Delta G^0 = GB(A)$

$-\Delta H^0 = PA(A)$

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International Journal of Mass Spectrometry and Ion Processes

A relationship between the kinetics and thermochemistry of proton transfer reactions in the gas phase

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Abstract

For the proton transfer reaction $[MH]^+ + B \rightarrow M + [BH]^+$ **(I)** a correlation is observed between the experimental reaction rate k_{exp} and the standard free energy variation ΔG°. This correlation may be described by a relationship of the type $k_{exp}/k_{coll} = 1/[1 + \exp(\Delta G^\circ + G_a^\circ)/RT]$ where k_{coll} is the collision rate constant and ΔG_a° an apparent energy barrier for reaction **(I)**. It is found that ΔG_a° is of the same order as RT and thus the preceding relationship allows the determination of unknown gas-phase basicities. Implications for the use of the "bracketing" and the "kinetic" methods are discussed.

Keywords: Bracketing and kinetic methods; Gas-phase; Kinetics and thermochemistry relationship; Proton affinity; Proton transfer

$$AH^+ + B \longrightarrow A + BH^+$$

$$\Phi = \frac{a}{1 + e^{[b(c - GB(B))]}}$$

Where: a = adjustement coefficient

b = 1/RT

c = GB(A) + ΔG^0_a

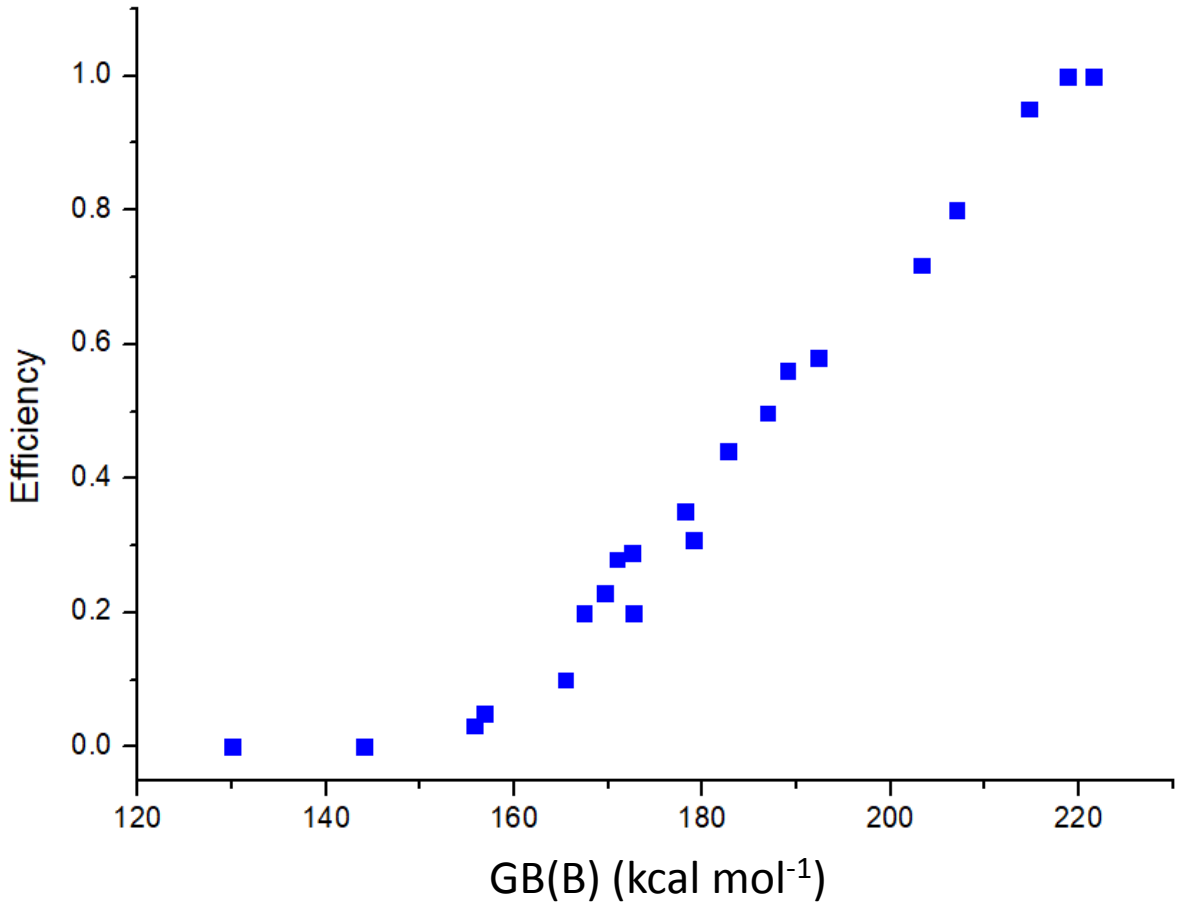
Apparent energy barrier for the reaction

$$GB(A) \approx c - \frac{1}{b}$$

$$\Delta G^0_a \approx RT$$

	GB (kcal/mol)	K_{exp}	K_{ADO}	Φ
CH_4	130	0	$1.02\ 10^{-09}$	0.00
COS	144	0	$1.08\ 10^{-09}$	0.00
C_2H_4	155.7	$3.30\ 10^{-11}$	$1.05\ 10^{-09}$	0.03
$(CF_3)_2CHOH$	156.8	$6.00\ 10^{-11}$	$1.20\ 10^{-09}$	0.05
CF_3COCH_3	165.4	$1.70\ 10^{-10}$	$1.70\ 10^{-09}$	0.10
CF_3CH_2OH	167.4	$2.44\ 10^{-10}$	$1.22\ 10^{-09}$	0.20
$CF_3CO_2CH_3$	169.6	$4.14\ 10^{-10}$	$1.80\ 10^{-09}$	0.23
$ClCH_2CN$	170.9	$6.20\ 10^{-10}$	$2.22\ 10^{-09}$	0.28
C_3H_6	172.7	$2.30\ 10^{-10}$	$1.15\ 10^{-09}$	0.20
CH_3NO_2	172.5	$6.58\ 10^{-10}$	$2.27\ 10^{-09}$	0.29
c-C_2H_4O	178.1	$5.90\ 10^{-10}$	$1.68\ 10^{-09}$	0.35
CH_3CN	179	$8.40\ 10^{-10}$	$2.72\ 10^{-09}$	0.31
$(CH_3)_2O$	182.7	$6.34\ 10^{-10}$	$1.44\ 10^{-09}$	0.44
Acetone	186.9	$1.01\ 10^{-09}$	$2.03\ 10^{-09}$	0.50
Methyl acetate	189	$8.85\ 10^{-10}$	$1.58\ 10^{-09}$	0.56
Dicyclopropylketone	192.3	$9.10\ 10^{-10}$	$1.57\ 10^{-09}$	0.58
2-methyloxipropene	203.3	$1.58\ 10^{-09}$	$2.20\ 10^{-09}$	0.72
Pyridine	207	$8.80\ 10^{-10}$	$1.10\ 10^{-09}$	0.80
4-picoline	214.7	$1.74\ 10^{-09}$	$1.83\ 10^{-09}$	0.95
2,5-lutidine	218.8	$2.00\ 10^{-09}$	$1.92\ 10^{-09}$	1.00

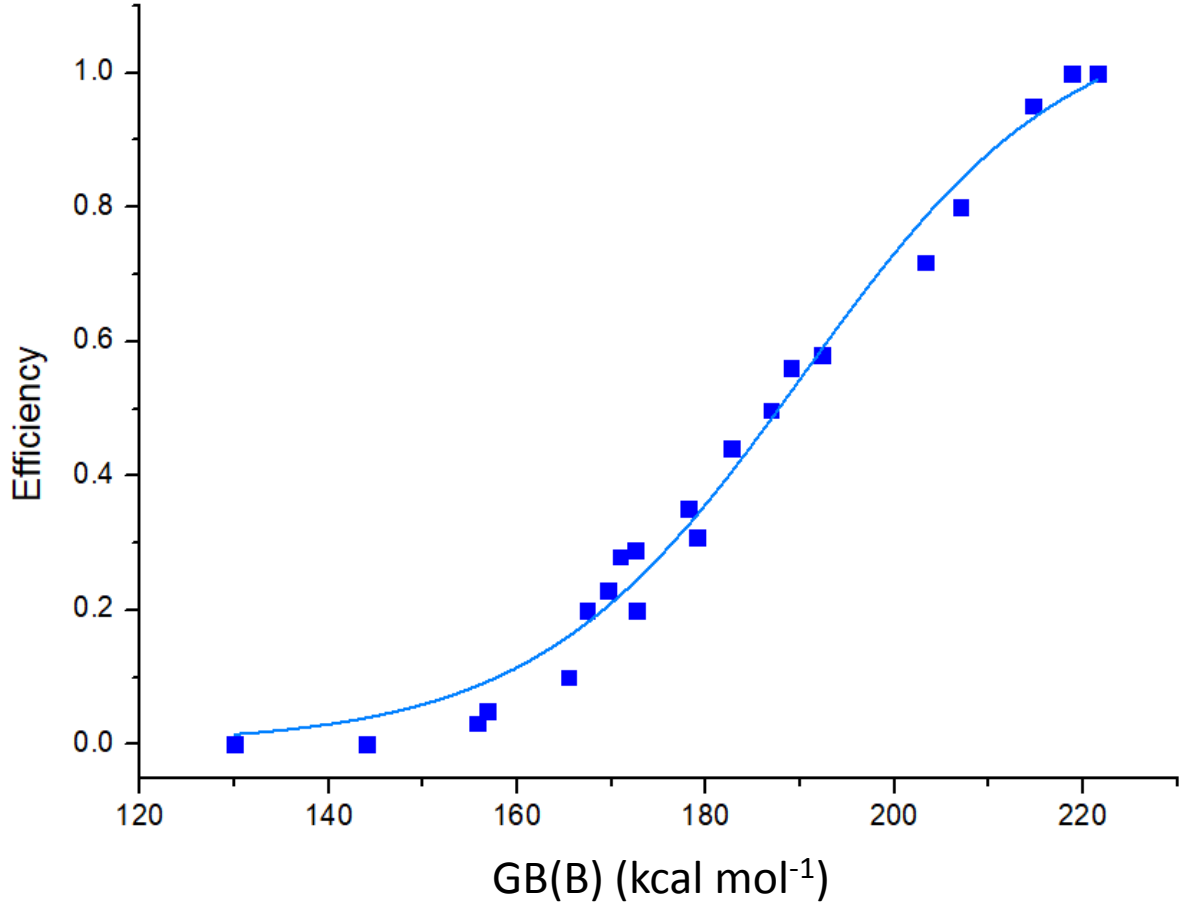
$$H_3SO_3^+ + B \longrightarrow H_2SO_3 + BH^+$$



$$H_3SO_3^+ + B \longrightarrow H_2SO_3 + BH^+$$

$$\Phi = \frac{a}{1 + e^{[b(c - GB(B))]}}$$

	Value	Standard Err
a	1.09618	0.05965
b	0.07103	0.00643
c	190.186	2.22651

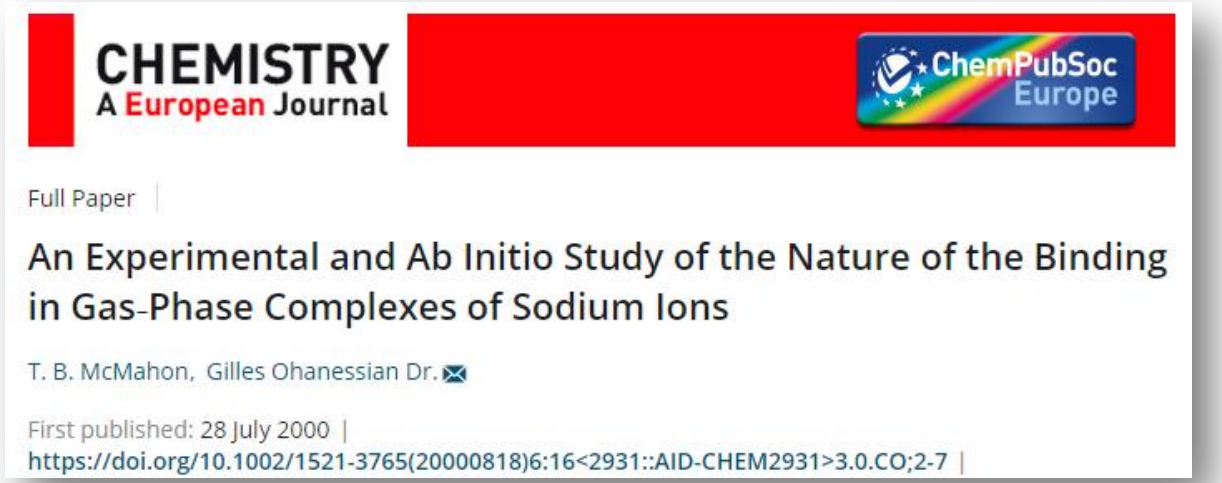


$$GB(H_2SO_3) = c - \frac{1}{b} = 176\ kcal\ mol^{-1}$$

Application for cation basicity

$$\Phi = \frac{a}{1 + e^{[b(c - CB(B))]}}$$

Known values for cation basicity for the neutrals of your choice are required!



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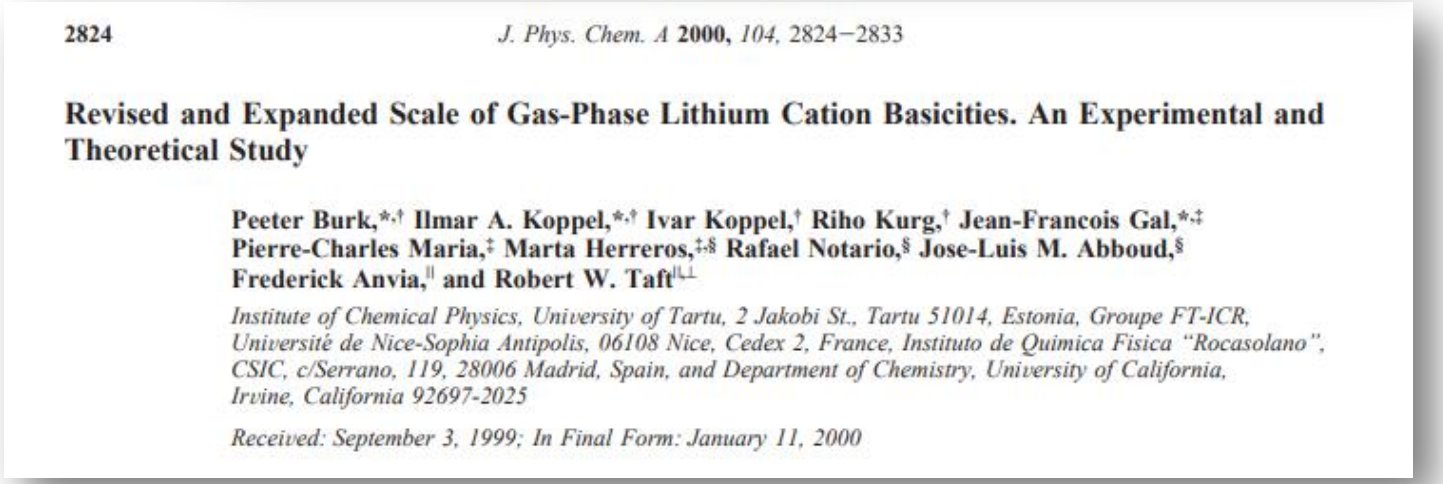
Full Paper

An Experimental and Ab Initio Study of the Nature of the Binding in Gas-Phase Complexes of Sodium Ions

T. B. McMahon, Gilles Ohanessian Dr.

First published: 28 July 2000 |
https://doi.org/10.1002/1521-3765(20000818)6:16<2931::AID-CHEM2931>3.0.CO;2-7 |



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Revised and Expanded Scale of Gas-Phase Lithium Cation Basicities. An Experimental and Theoretical Study

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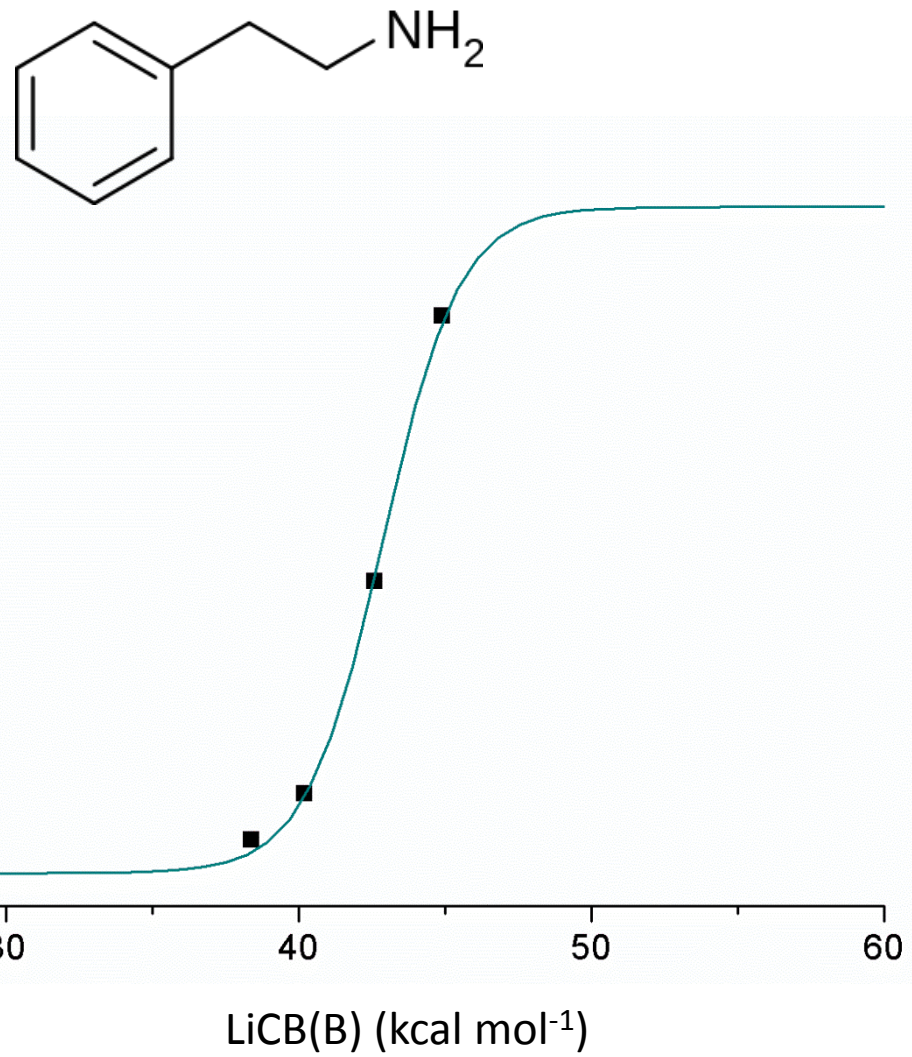
$$[Ph(CH_2)_2NH_2Li]^+ + B \longrightarrow Ph(CH_2)_2NH_2 + [BLi]^+$$

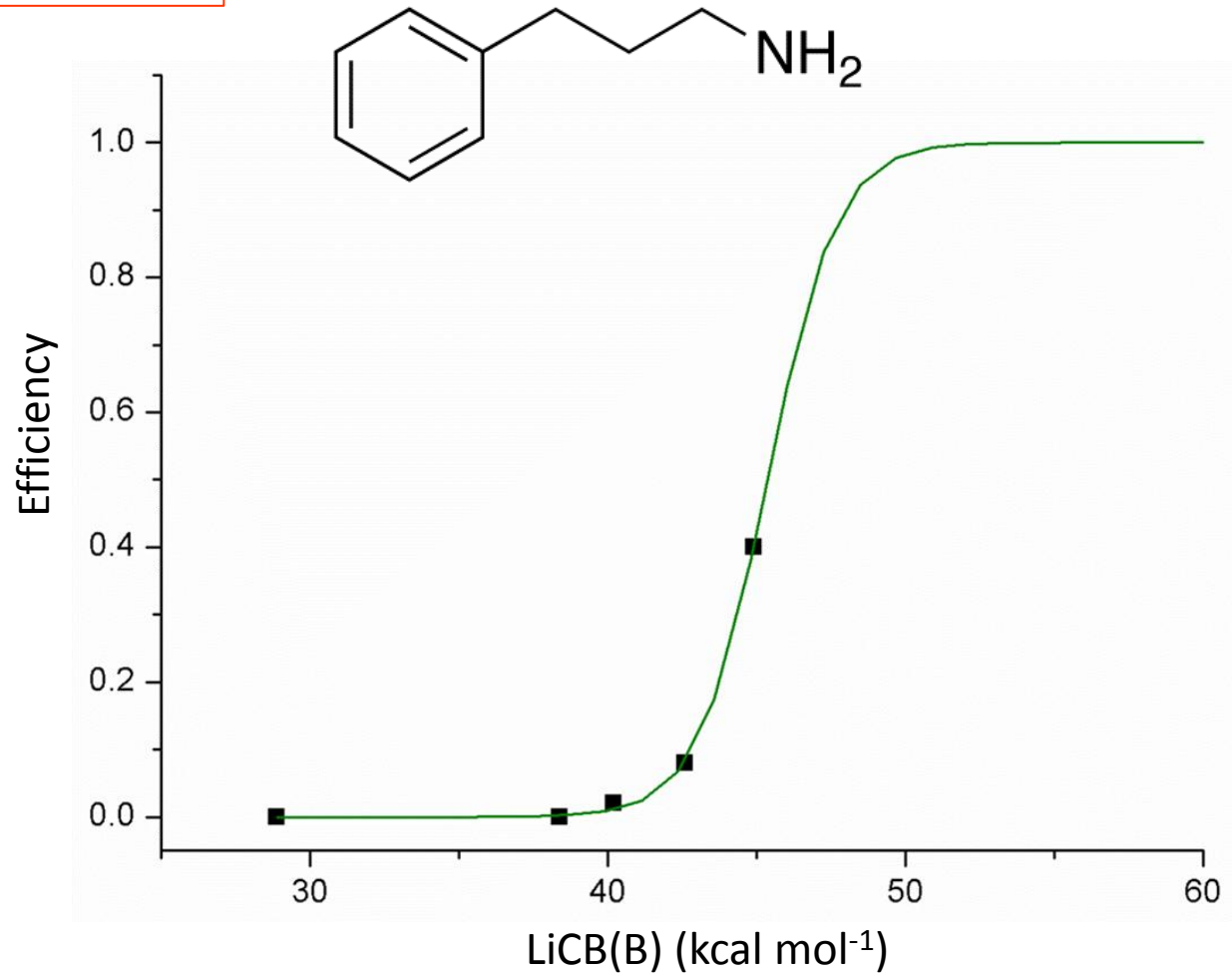
	LiCB (kcal/mol)	Φ
$CF_3CO_2CH_3$	28.9	0.00
$(cPr)_2CO$	38.4	0.05
1-methylimidazole	40.2	0.12
$MeOCH_2CH_2OH$	42.6	0.44
$(CH_2OMe)_2$	44.9	0.84



$$LiCB(Ph(CH_2)_2NH_2) = c - \frac{1}{b} = 42\ kcal\ mol^{-1}$$

$$[Ph(CH_2)_3NH_2Li]^+ + B \longrightarrow Ph(CH_2)_3NH_2 + [BLi]^+$$

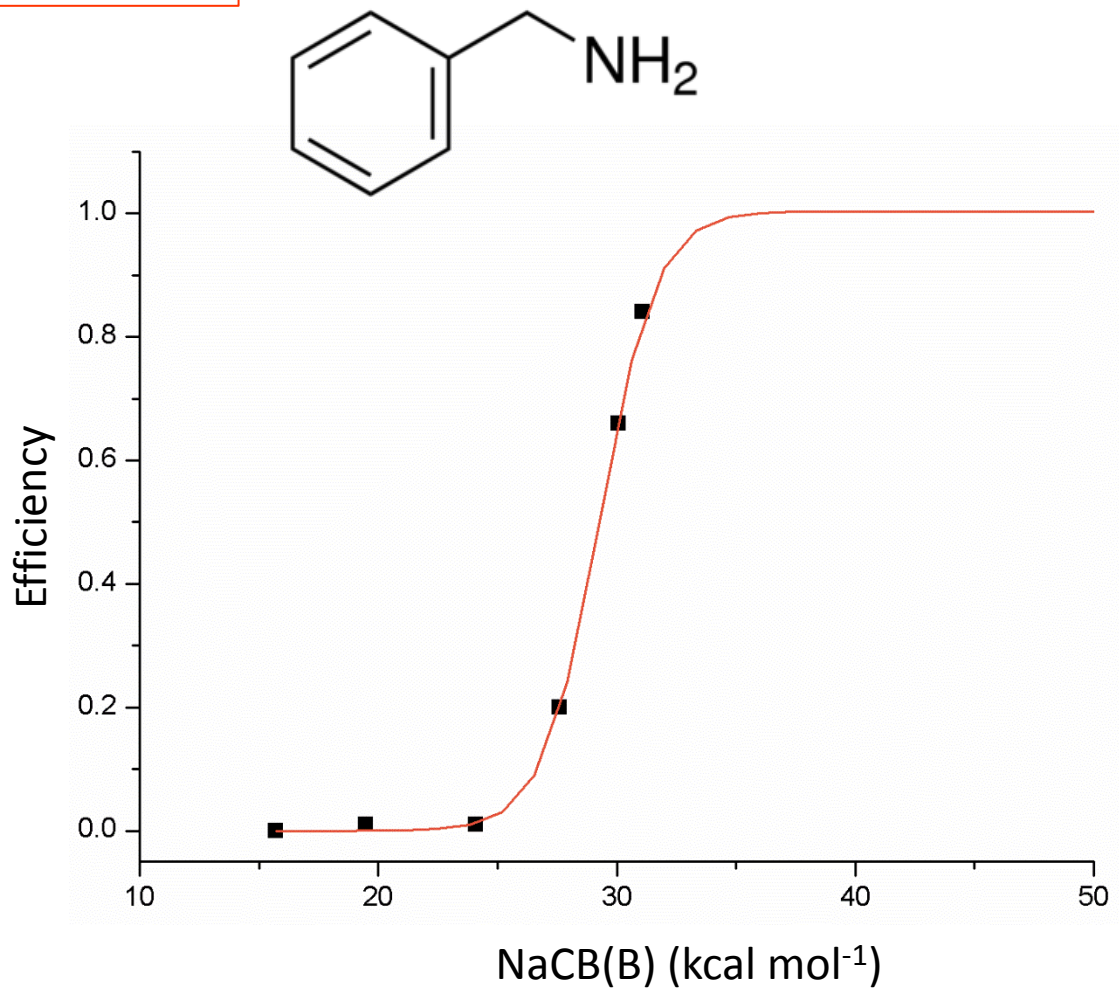
	LiCB (kcal/mol)	Φ
$CF_3CO_2CH_3$	28.9	0.00
$(cPr)_2CO$	38.4	0.05
1-methylimidazole	40.2	0.02
$MeOCH_2CH_2OH$	42.6	0.08
$(CH_2OMe)_2$	44.9	0.40



$$LiCB(Ph(CH_2)_3NH_2) = c - \frac{1}{b} = 44\ kcal\ mol^{-1}$$

$$[PhCH_2NH_2Na]^+ + B \longrightarrow PhCH_2NH_2 + [BNa]^+$$

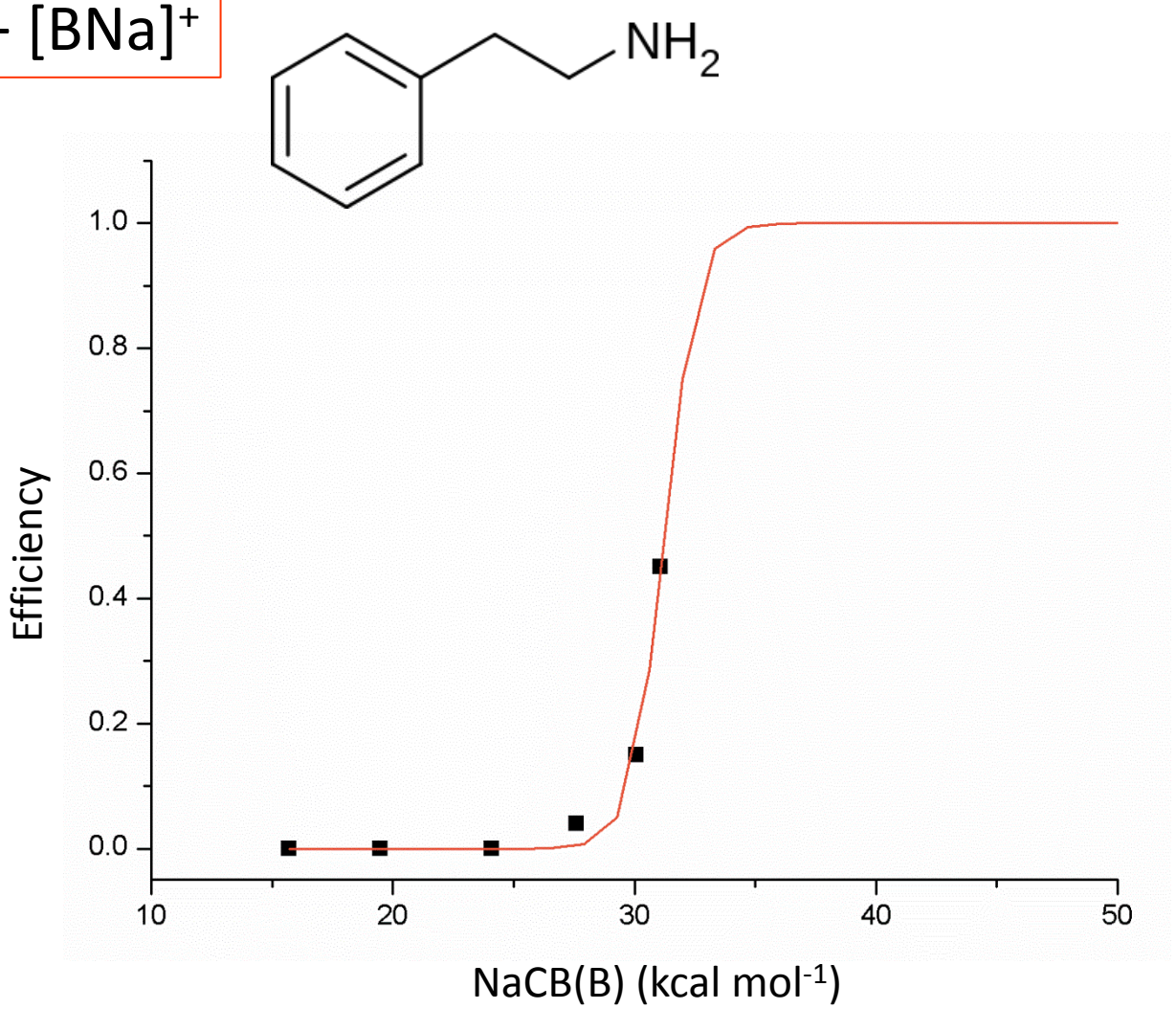
	NaCB (kcal/mol)	Φ
C_6H_6	15.7	0.00
Methylamine	19.5	0.01
Acetone	24.1	0.01
$CH_2(OC_2H_5)_2$	27.6	0.20
$HCON(CH_3)_2$	30.1	0.67
$(CH_2OMe)_2$	31.1	0.84



$$NaCB(PhCH_2NH_2) = c - \frac{1}{b} = 28\ kcal\ mol^{-1}$$

$$[Ph(CH_2)_2NH_2Na]^+ + B \longrightarrow Ph(CH_2)_2NH_2 + [BNa]^+$$

	NaCB (kcal/mol)	Φ
C_6H_6	15.7	0.00
Methylamine	19.5	0.00
Acetone	24.1	0.00
$CH_2(OC_2H_5)_2$	27.6	0.04
$HCON(CH_3)_2$	30.1	0.15
$(CH_2OMe)_2$	31.1	0.45



$$NaCB(Ph(CH_2)_2NH_2) = c - \frac{1}{b} = 30\ kcal\ mol^{-1}$$